

Micro-canonical thermodynamics: Why does heat flow from hot to cold.

Hans Henrik Rugh

Department of Mathematics, University of Paris-Sud 11, FR-91405 Orsay, France

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We show how to use a central limit approximation for additive co-cycles to describe non-equilibrium and far from equilibrium thermodynamic behaviour. We consider first two weakly coupled Hamiltonian dynamical systems initially at different micro-canonical temperatures. We describe a stochastic model where the energy-transfer between the two systems is considered as a random variable satisfying a central limit approximation. We show that fluctuations in energy observables are linearly related to the heat-transfer (dissipation). As a result, on average, heat flows from hot to cold. We also consider the far from equilibrium situation of a non-Hamiltonian thermostatted system as in Evans et al. *Phys. Rev. Lett.* **71**, 2401 (1993). Applying the same central limit approximation we re-derive their relation for the violation of the 2nd law of thermodynamics. We note that time-reversal symmetry is not used in our derivation.

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Starting with the pioneering work of Boltzmann, equilibrium statistical mechanics has developed into a solid corner-stone of theoretical physics. Using perturbative expansions, Kubo considered systems close to equilibrium and obtained fluctuation-dissipation theorems, relating dissipation (linear response) in the system to fluctuations described by decay of correlation functions. We refer to e.g. [7] for a nice review. Of great current interest, but less understood, is the case of far from equilibrium statistical mechanics. Recent approaches to the subject were initiated by Evans et al. [2] (see also [5] for a review). One considers a thermostatted system driven by external forces. The thermostat gives rise to a phase space contraction which is interpreted as a production of entropy. Through numerical simulations, Evans et al. made the interesting observation that the 2nd law of thermodynamics is broken in a systematic way. As a model for this phenomena the authors suggest that the dynamical behavior resembles that of the attractor of an Anosov flow with an underlying time-reversal symmetry. This model has then been further developed by e.g. Gallavotti and Cohen [3]. We also refer to Kurchan [6] and Lebowitz and Spohn [8] for a somewhat different stochastic approach (but still using an inherent time-reversal symmetry). Bustamante et al. [1] (see also references therein) gives a review of recent physical experiments supporting the theoretical work.

Our aim below is to provide an elementary description of not only the above mentioned phenomena, but also the time evolution of the energy transfer between two weakly coupled hamiltonian systems. Neither thermostats nor external forces are involved in this latter case. Our arguments are based upon a strong stochastic assumption, namely that a central limit approximation applies to so-called additive co-cycles in the systems. In particular, we do not need the presence of a time-reversal symmetry. As in [2] we obtain in both cases a universal law for the violation of the 2nd law of thermodynamics. Our approach is closely related to the study of the "structure functions" which were used by Zwanzig [12].

TWO SYSTEMS AND A WEAK INTERACTION

Consider hamiltonians H_1 and H_2 on phase spaces Ω_1 and Ω_2 , respectively. We will study the energy flow between the two systems that arises from introducing a weak coupling U_{12} defined on the product space, $\Omega_1 \times \Omega_2$. When the (micro-canonical) temperatures of the two systems are different one expects on heuristic grounds that energy should flow from the 'hotter' to the 'colder' system. We wish to quantify this phenomenon within the micro-canonical ensemble and without introducing external forces, not heat-baths in the problem. Recall, that the flow ϕ^t associated to the total Hamiltonian function $H = H_1 + H_2 + U_{12}$ preserves the total energy as well as the product Liouville volume $m(d\xi) = m_1(d\xi_1)m_2(d\xi_2)$, with $\xi = (\xi_1, \xi_2)$ being coordinates on $\Omega_1 \times \Omega_2$. In particular, also the micro-canonical measure $\mu_E(d\xi) = \delta(H(\xi) - E)m(d\xi)$ having support on the energy surface $H(\xi) = E$ is invariant under the flow. Our goal is to study the time evolution of e.g. the first system, H_1 under the global flow ϕ^t at some fixed total energy E . We will adapt a stochastic point of view. The basic idea is that when the coupling is weak and each sub-system (hopefully) is mixing fast enough on its proper energy surface then at every instant of time each system is close to an equilibrium of that system. In spirit this is close to linear response theory. There, however, one usually applies a fixed (small) perturbation and then lets the system evolve to a new equilibrium state close to the original. In our context we consider a slow but steady evolution away from the original state. Instead of starting out at a particular

point in phase space we start out with an H_1 -conditional ensemble at time $t = 0$:

$$\delta(H_1(\xi) - E_1)\mu_E(d\xi).$$

The normalizing factor,

$$e^{f(E_1)} = \int \delta(H_1(\xi) - E_1)\mu_E(d\xi),$$

defines the E_1 -conditional entropy, $f(E_1)$. Now, this conditional ensemble is, in general, not time-invariant when the interaction is turned on. At time $t > 0$, the probability distribution of the values of $H_1(\phi^t(\xi))$ will be given by an expression of the form :

$$p_t(x|E_1) = \frac{\int \delta(H_1(\phi^t(\xi)) - x) \delta(H_1(\xi) - E_1) \mu_E(d\xi)}{\int \delta(H_1(\xi) - E_1) \mu_E(d\xi)}$$

We assume for simplicity of notation that the distribution admits a density. More generally one could formulate the relation in terms of measures without affecting the conclusions. By normalization, the kernel satisfies:

$$\int p_t(x|E_1) dx = 1.$$

It verifies, however, another important identity: Multiplying by $e^{f(E_1)}$ and integrating with respect to E_1 we get

$$\begin{aligned} \int p_t(x|E_1) e^{f(E_1)} dE_1 &= \int \delta(H_1(\phi^t(\xi)) - x) \mu_E(d\xi) \\ &= \int \delta(H_1(\xi) - x) \mu_E(d\xi) \\ &= e^{f(x)}, \end{aligned} \tag{1}$$

where we used the fact that $\mu_E(d\xi)$ is ϕ^t -invariant. At present the above expressions are exact.

We come to the crucial approximation: Consider $X_t = H_1(\phi^t(\xi))$ as a random variable whose probability distribution is given by $p_t(x|E_1)dx$. The mean drift is $m_t(E_1) = \mathbf{E}(X_t) - E_1 = \int (x - E_1) p_t(x|E_1) dx$ and the variance is $\sigma_t^2(E_1) = \text{Var}(X_t)$. Both drift and variance are functions of t and E_1 . When t tends to zero, $p_t(x|E_1) \rightarrow \delta(x - E_1)$ and when t tends to infinity (assuming global mixing) $p_t(x|E_1) \rightarrow e^{f(x)} \times \text{const}$. The energy increment $A^t(\xi) = H_1(\phi^t(\xi)) - H_1(\xi)$ is an ‘additive co-cycle’. By this we mean that for all $s, t \geq 0$, $\xi \in \Omega_1 \times \Omega_2$:

$$A^{t+s}(\xi) = A^t \circ \phi^s(\xi) + A^s(\xi). \tag{2}$$

When time-correlations decay fast enough, such additive co-cycles tend to have asymptotic properties in common with sums of independent random variables. In particular, it may be within reason to assume that it behaves like a gaussian variable (at least on certain time scales). This is the case e.g. when looking at smooth observables in Anosov systems or in exponentially mixing Markov chains.

Central Limit Approximation: Assume that there are two characteristic time-scales $\tau_{\text{mix}} \ll T_{\text{eq}}$ where τ_{mix} is a ‘mixing’-time of the sub-systems and T_{eq} is a time-scale for ‘significant’ changes in the energy of each sub-systems. When $\tau_{\text{mix}} \ll t \ll T_{\text{eq}}$ we may approximate $p_t(x|E_1)$ by the corresponding normal distribution:

$$p_t(x|E_1) \approx \frac{1}{\sqrt{2\pi}\sigma_t} \exp\left(-\frac{(x - E_1 - m_t)^2}{2\sigma_t^2}\right). \tag{3}$$

Weak Coupling Approximation: We need to be able to calculate derivatives of the relative entropy $f(x)$. This is easy if we can neglect the interaction term. In this approximation $H(\xi) = H_1(\xi_1) + H_2(\xi_2)$ and

$$\begin{aligned} e^{f(x)} &= \int \delta(H_1(\xi_1) - x) \mu_E(d\xi) \\ &= \int \delta(H_1(\xi_1) - x) \delta(H_1(\xi_2) - (E - x)) m_1(d\xi_1) m_2(d\xi_2) \\ &= e^{S_1(x) + S_2(E-x)}, \end{aligned} \tag{4}$$

where $S_i(x) = \log \int \delta(H_i(\xi_i) - x) m_i(d\xi_i)$, $i = 1, 2$ are the μ -canonical entropies of the two sub-systems. For each sub-system, one may associate its μ -canonical temperature, i.e. $\frac{1}{T_1} = \frac{\partial S_1}{\partial E_1}$ as well as its heat-capacity $\frac{1}{C_1} = \frac{\partial T_1}{\partial E_1} = -T_1^2 \frac{\partial^2 S_1}{\partial E_1^2}$. As we showed in earlier papers [10, 11], such quantities are computable within the μ -canonical ensemble provided each subsystem is ergodic. On the time-scale $\tau_{\text{mix}} \ll t \ll T_{\text{eq}}$, one may assign local micro-canonical thermodynamic characteristics to each sub-system. In the weak coupling limit the global equilibrium of the combined system is at the energy $E_1 = E_1^{\text{eq}}$ for which $f'(E_1^{\text{eq}}) = 0$ or $T_1(E_1^{\text{eq}}) = T_2(E - E_1^{\text{eq}})$, i.e. the two micro-canonical temperatures are equal. When heat-capacities are positive (i.e. S_1 and S_2 are strictly concave) the corresponding energy is unique. But we do not need this for the present discussion.

Recall that the distribution p_t function for X_t leaves the micro-canonical ensemble invariant:

$$\int p_t(x|E_1) e^{f(E_1)} dE_1 = e^{f(x)}.$$

When t is not too large it is reasonable to expect the variance of X_t to be small compared to the inverse of the curvature of f . We may then replace $f(E_1)$ by its first order Taylor expansion around x : $f(E_1) - f(x) = \lambda(E_1 - x) + o(E_1 - x)$ with $\lambda = f'(x) = \frac{1}{T_1(x)} - \frac{1}{T_2(E - x)}$. We insert this our central limit expression (3) and get for the integral:

$$\int \exp\left(-\frac{(x - E_1 - m_t)^2}{2\sigma_t^2} + \lambda(E_1 - x)\right) dE_1 = \exp(\lambda^2 \sigma_t^2 / 2 - \lambda m_t) = 1.$$

This implies that either $\lambda = 0$ (which corresponds to the systems having identical temperatures, i.e they are in thermodynamic equilibrium) or, more interestingly, when λ is non-zero we get the relation $m_t = \frac{1}{2} \lambda \sigma_t^2$. We have obtained the following:

Fluctuation Dissipation Relation. Under the Central Limit Approximation we have for $\tau_{\text{mix}} \ll t \ll T_{\text{eq}}$:

$$m_t(E_1) = \frac{1}{2} \sigma_t^2(E_1) \left(\frac{1}{T_1(E_1)} - \frac{1}{T_2(E - E_1)} \right). \quad (5)$$

$$\log \frac{p_t(E_1 + u | E_1)}{p_t(E_1 - u | E_1)} = \frac{2m_t}{\sigma_t^2} u = \left(\frac{1}{T_1(E_1)} - \frac{1}{T_2(E - E_1)} \right) u. \quad (6)$$

The first equality states that the mean drift in energy (dissipation) of each sub-system is proportional to the fluctuations in the sub-system with a constant of proportionality being the difference of the inverse temperatures of the two systems. Since fluctuations are non-negative, on average energy flows from ‘hot’ to ‘cold’. The second equality is obtained by combining expression (3) and the fluctuation dissipation relation (5). It expresses the relative probability of a violation of the 2nd law of thermodynamics at certain time and energy scales.

VALIDITY AND COMPUTABILITY

Estimates both for $p_t(x|E_1)$ and temperatures may be obtained through numerical simulations thus allowing for a verification of our Central Limit Approximation (CLA) as well as the Fluctuation Dissipation Relation (FDR). Assuming ergodicity it suffices for $p_t(x|E_1)$ to run the system without interactions to get initial points representing the H_1 -conditional ensemble, then turn on the (weak) interaction and run the ensemble to give estimates for this transition probability. For the temperatures of the sub-systems, we may e.g. use [10, 11] : If \mathbf{X}_i , $i = 1, 2$ are vector fields on $T\Omega_i$ for which $dH_i(\mathbf{X}_i) \equiv 1$ then, without interactions, we have $1/T_i = \langle \text{div}_{m_i}(\mathbf{X}_i) | E_i \rangle$, the ergodic average of the observable $\text{div}_{m_i}(\mathbf{X}_i)$ at energy E_i for each sub-system. Under weak interactions but assuming that sub-system energies varies slowly compared to its ergodic averaging, such expressions are good candidates for temperature observables for the two sub-systems.

For numerical reasons, interactions should be small but not too small. The interaction constitute background fluctuations of order $\omega = \mathcal{O}(U_{12})$. If this is too large, it is unlikely that one may observe the FD-relation. On the other hand energy exchange is a second order phenomena (see e.g. [12]) so we have to wait a time of order $1/\omega$ to get an effective energy transfer exceeding the background noise. Numerical errors could then create problems.

The expression (3) for $p_t(x|E_1)$ could be a good approximation even on time scales smaller than the mixing time of sub-systems. The reason is that for a large system space mixing may give rise to a good central limit approximation for the observable H_1 even without time-mixing. The FDR may, however, fail in that case. As a (non-generic, though) example suppose that system 2 itself is a sum of two sub-systems with a small interaction: $H_2 = H_a + V_{ab} + H_b$. We now add an interaction of the form $U_{12} = U_{1,a} - V_{ab}$ to $H_1 + H_2$. This has the effect of coupling H_1 and H_a but decoupling their sum from H_b . As a result there will be fluctuations in H_1 but the predicted mean drift will in general be wrong, there will be no global equilibration and the fluctuation dissipation relation as stated should fail.

A THERMOSTATED NON-EQUILIBRIUM SYSTEM

We now consider a situation as described in [2] in which the authors consider a Hamiltonian H on a phase space Ω and subjected to a thermostat. One associates to this a non-Hamiltonian vector field X_H and its flow ϕ^t . For details of the construction see [2]. For our purposes, the essential properties may be summarized as follows: The Hamiltonian flow ϕ^t preserves H but not the Liouville space volume m . We write $\mu_E = \delta(H - E)m$ for the associated area form on the energy surface. Neither m , nor μ_E is invariant under X_H . The Jacobian $\text{Jac}^t(\xi) = m(\phi^t d\xi)/m(d\xi)$ describes the volume transformation along the flow. Because of H -invariance we have $\text{Jac}^t(\xi) = \mu_E(\phi^t dA)/\mu_E(dA)$ as well, i.e. it is the same Jacobian for the surface area and for the bulk volume. To see this one may e.g. use differential forms and take the Lie derivative of μ_H : $L_{X_H}(\delta(H - E)m) = \delta(H - E)L_{X_H}m = \delta(H - E)\text{div}_m(X_H)m$, where the first equality is due to $L_X H = dH(X) = 0$. It shows that infinitesimally m and μ_E have the same Jacobian so this is also the case for the flow.

One wants to observe the phase space contraction rate, manifested by the above Jacobian. The Jacobian is multiplicative and not additive but taking a logarithm, we get an additive co-cycle as before. So, our observable will be $A^t = \log \text{Jac}^t(\xi)$, which verifies $A^{t+s} = A^t \circ \phi^s + A^s$. It is a computable, i.e. observable quantity in this context. The object of interest is then the distribution function for A^t which we consider in the μ_E -ensemble:

$$p_t(\alpha) = \frac{\int_{\Omega} \delta(A^t(\xi) - \alpha) \mu_E}{\int_{\Omega} \mu_E}.$$

Since $\phi^t : \Omega \rightarrow \Omega$ is a diffeomorphism we get by change of variables:

$$\int_{\Omega} \mu_E = \int_{\phi^t \Omega} \mu_E = \int_{\Omega} \text{Jac}^t(\xi) \mu_E(\xi).$$

Inserting the distribution function for A^t we get the (exact) relation:

$$1 = \frac{\int_{\Omega} \text{Jac}^t(\xi) \mu_E(\xi)}{\int_{\Omega} \mu_E(\xi)} = \int e^{\alpha} p_t(\alpha) d\alpha.$$

This is a constraint equation for the distribution function p_t . As A_t is an additive co-cycle we again make the strong stochastic assumption that we may approximate p_t by a normal distribution, $p_t \sim \mathcal{N}(m_t, \sigma_t^2)$. Doing so and inserting in the above constraint equation yields $\exp(m_t + \sigma_t^2/2) = 1$ or $m_t = -\sigma_t^2/2$. This is the FD relation of e.g. [2, 3]. And as in these cited papers one has the symmetry-relation

$$p_t(\alpha)/p_t(-\alpha) = e^{\alpha}.$$

There is an important approximation taking place when comparing the above derivation and the numerical simulations. In our derivation the distribution of the observable A_t is with respect to the initial distribution $\mu_E = \delta(H - E)m$ whereas the numerical computations are done for a (hopefully) stationary state of the system. This distinction also makes a subtle difference in the point of view of [2] and [3]. For an Anosov system, the distinction is not important. In both ensembles a central limit approximation hold and with the same constants. Working in the stationary state, however, is numerically more stable as it eliminates the contribution of transients which can be quite large. For more realistic models, it would be of interest to compare numerically the two ensemble distributions.

We note that time-reversal symmetry is not needed in the above derivation. Again it would be interesting to compare with numerical simulations for a system without time-reversal symmetry. Mittag et al presented such a system in [4] for which the distribution function p_t was quite far from gaussian and the FD-relation fails. This, however, does not contradict the above derivation since in their case the external field was changed during the time

span of the experiment. A^t is then not an additive co-cycle so transient behaviour becomes significant. We also note that our derivation does not make use of the underlying symplectic structure of phase space. So in principle our derivation makes sense for any dynamical system on a compact manifold (here, $\{H = E\}$) that converges fast enough towards a natural measure and for which correlations decay fast enough.

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